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## New views on “old” carbon in the Amazon River: Insight from the source of organic carbon eroded from the Peruvian Andes

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[1] Mountain rivers play a key role in the delivery of particulate organic carbon (POC) to large river systems and the ocean. Due to the extent of its drainage area and runoff, the Amazon River is one of Earth's most important biogeochemical systems. However, the source of POC eroded from the humid region of the Eastern Andes and the input of fossil POC from sedimentary rocks ( $\text{POC}_{\text{fossil}}$ ) remains poorly constrained. Here we collected suspended sediments from the Kosñipata River during flood events to better characterize Andean POC, measuring the nitrogen to organic carbon ratio (N/C), stable carbon isotopes ( $\delta^{13}\text{C}_{\text{org}}$ ) and radiocarbon ( $\Delta^{14}\text{C}_{\text{org}}$ ).  $\Delta^{14}\text{C}_{\text{org}}$  values ranged from  $-711\text{‰}$  to  $-15\text{‰}$ , and significant linear trends between  $\Delta^{14}\text{C}_{\text{org}}$ , N/C and  $\delta^{13}\text{C}_{\text{org}}$  suggested that this reflects the mixing of  $\text{POC}_{\text{fossil}}$  with very young organic matter ( $\Delta^{14}\text{C}_{\text{org}} \sim 50\text{‰}$ ) from the terrestrial biosphere ( $\text{POC}_{\text{non-fossil}}$ ). Using N/C and  $\Delta^{14}\text{C}_{\text{org}}$  in an end-member mixing analysis, we quantify the fraction of  $\text{POC}_{\text{fossil}}$  (to within 0.1) and find that it contributes a constant proportion of the suspended sediment mass ( $0.37 \pm 0.03\%$ ) and up to 80% of total POC. In contrast, the relative contribution of  $\text{POC}_{\text{non-fossil}}$  was variable, being most important during the rising limb and peak discharges of flood events. The new data shed light on published measurements of “old” POC (low  $\Delta^{14}\text{C}_{\text{org}}$ ) in Andean-fed tributaries of the Amazon River, with their  $\Delta^{14}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values consistent with variable addition of  $\text{POC}_{\text{fossil}}$ . The findings suggest a greater persistence of Andean POC in the lowland Amazon than previously recognized.

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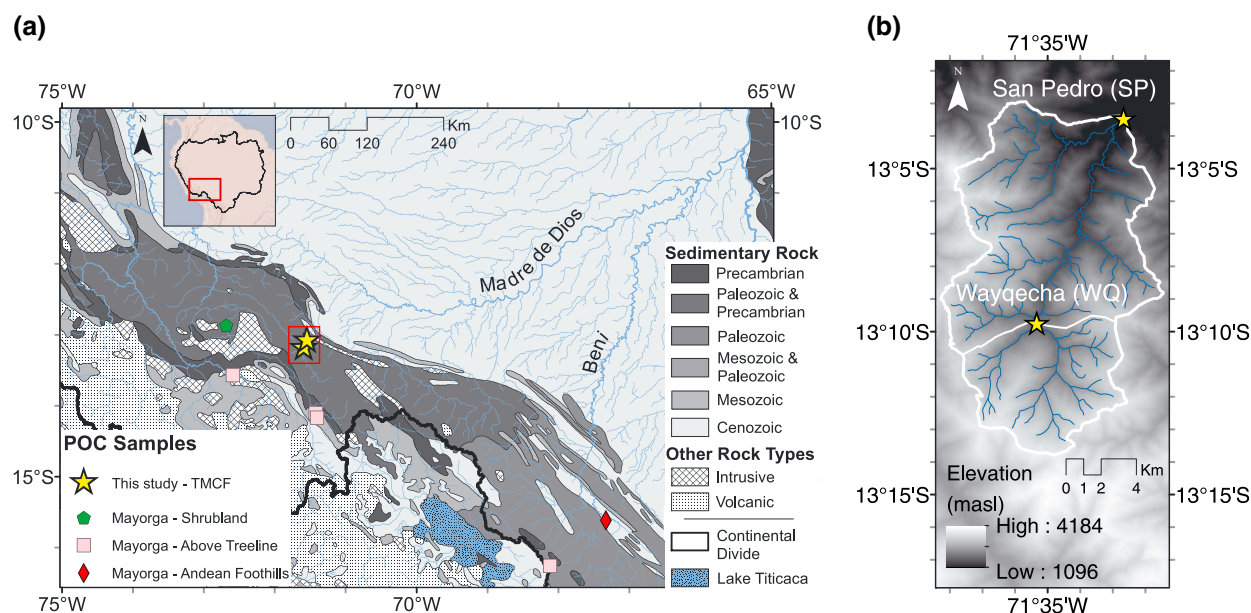
## 1. Introduction

[2] Mountain rivers are an important component of the world’s major river basins and play a crucial role in lowland river biogeochemistry and carbon cycling [Gibbs, 1967; Hedges *et al.*, 2000; Galy *et al.*, 2008b; McClain and Naiman, 2008]. High rates of physical erosion can result in the efficient transfer of particulate organic carbon (POC) by rivers [Kao and Liu, 1996; Stallard, 1998; Hilton *et al.*, 2012] which are also dominant sources of clastic sediment from the continents [Milliman and Syvitski, 1992]. The association of POC with mineral sediment can inhibit its degradation during transport and deposition [Canfield, 1994; Hedges and Keil, 1995]. As a result, mountain rivers can contribute importantly to the transfer of POC to large river systems [Hedges *et al.*, 1986a; Galy and Eglinton, 2011] and in the delivery of POC to the ocean [Lyons *et al.*, 2002]. Constraining the source of this POC is fundamental to understanding how its erosion and transfer impacts carbon cycling. Mountain rivers can transport POC eroded from the terrestrial biosphere (POC<sub>non-fossil</sub>), recently fixed via photosynthesis from atmospheric CO<sub>2</sub> [e.g., Hilton *et al.*, 2008b]. POC<sub>non-fossil</sub> transfer exports a fraction of gross primary productivity [Malhi, 2012] and if it escapes oxidation during transport [Mayorga *et al.*, 2005; Cole *et al.*, 2007; Tranvik *et al.*, 2009] and is buried in long-lived floodplain sediments [e.g., Stallard, 1998; Aalto *et al.*, 2003] or offshore [e.g., Galy *et al.*, 2007b] can be a net sink of atmospheric CO<sub>2</sub> [France-Lanord and Derry, 1997]. At the same time, physical erosion can mobilize older POC [Galy and Eglinton, 2011; Pawson *et al.*, 2012] which if oxidized may counter contemporary CO<sub>2</sub> drawdown [e.g., Galy *et al.*, 2008a; Bouchez *et al.*, 2010]. In mountain rivers, fossil organic carbon from sedimentary bedrock (POC<sub>fossil</sub>) can be significant [Kao and Liu, 1996; Blair *et al.*, 2003; Leithold *et al.*, 2006; Hilton *et al.*, 2011a], having a marked

impact on the elemental and isotopic composition of particulate organic matter [Komada *et al.*, 2004; Galy *et al.*, 2007a; Hilton *et al.*, 2010].

[3] The Amazon River is the world’s largest fluvial system in terms of drainage area and runoff [Meybeck and Ragu, 1997]. It delivers 550–1500 Mt yr<sup>−1</sup> of sediment to the Atlantic [Meade *et al.*, 1979; Richey *et al.*, 1986; Dunne *et al.*, 1998; Guyot *et al.*, 2005; Martinez *et al.*, 2009] and is the largest point source of POC to the oceans, at ~15 MtC yr<sup>−1</sup> [Richey *et al.*, 1990; Beusen *et al.*, 2005]. The mountain headwaters in the Andes impart a strong signature on the inorganic chemistry of the particulate load [Allegre *et al.*, 1996; Gaillardet *et al.*, 1997; Bouchez *et al.*, 2011] and are thought to supply ~80–90% of the Amazon River’s sediment flux [Gibbs, 1967; Meade *et al.*, 1985; Richey *et al.*, 1986; Wittmann *et al.*, 2011]. In contrast, the majority of POC carried in the lowland Amazon River is thought to derive from floodplain sources [Mayorga *et al.*, 2005], which implies substantial replacement or consumption of Andean POC contributing to outgassing [Richey *et al.*, 2002].

[4] Andean riverine POC has been sampled in the upper Ucayali and upper Beni Rivers [Hedges *et al.*, 2000; Mayorga *et al.*, 2005; Aufdenkampe *et al.*, 2007; Townsend-Small *et al.*, 2007; Townsend-Small *et al.*, 2008]; however, large portions of the Andes remain un-sampled (e.g., the Madre de Dios River draining the Peruvian Andes) and the composition of Andean POC is poorly constrained in comparison to other mountain belts [Galy *et al.*, 2008b; Hilton *et al.*, 2010]. This makes it difficult to assess the fate of Andean POC during transport in the Amazon Basin. Rivers draining the Andes are known to receive significant input of clastic material from sedimentary rocks [Allegre *et al.*, 1996; Gaillardet *et al.*, 1997; Bouchez *et al.*, 2011] and it follows that POC<sub>fossil</sub> should be an important component of the suspended load



**Figure 1.** (a) Geological Map of study region in Peru [Schenk *et al.*, 1999] with an inset map of the Amazon Basin with the map area indicated. The stars represent the locations of gauging stations on the Kosñipata River valley (this study) and locations of published Andean POC data are shown by other symbols. (b) Kosñipata River valley, Peru with elevation (SRTM) and locations of hydrometric and sampling gauging stations.

[Komada *et al.*, 2004; Leithold *et al.*, 2006; Galy *et al.*, 2007a; Hilton *et al.*, 2008b; 2010]. A small number of radiocarbon measurements ( $n=4$ ) from the Beni River confirm this [Bouchez *et al.*, 2010] and demonstrate that the input of  $\text{POC}_{\text{fossil}}$  and its elemental and isotopic composition in the Amazon Basin requires renewed focus.

[5] Here we address these knowledge gaps in headwaters of the Peruvian Andes. The study focuses on the highly productive tropical montane cloud forest of a small mountain catchment draining sedimentary bedrock representative of a wider region draining to the Ucayali and Madeira Rivers, major Amazon tributaries (Figures 1a and 1b). To better constrain the compositional range of Andean POC, we employed a nested catchment approach in the Kosñipata River at 2250 meters above sea level (masl) and 1360 masl and collected suspended sediments at high temporal frequency (three-hourly). This strategy was designed to capture flood events sampling at times when the composition of POC can vary widely in mountain rivers [e.g., Hilton *et al.*, 2008b; Smith *et al.*, 2013]. To constrain the sources of POC, we have measured a combination of element ratios (nitrogen to organic carbon ratio, N/C), stable isotopes ( $\delta^{13}\text{C}_{\text{org}}$ ) and the radiocarbon content of POC ( $\Delta^{14}\text{C}_{\text{org}}$ , ‰). The approach permits a detailed investigation of  $\text{POC}_{\text{fossil}}$  input and its quantification in mountain rivers [Kao and Liu, 2000; Komada *et al.*, 2004; Leithold *et al.*, 2006; Hilton *et al.*, 2008b; 2010]. Following an

end-member mixing analysis using N/C and  $\Delta^{14}\text{C}_{\text{org}}$ , the timing of  $\text{POC}_{\text{non-fossil}}$  and  $\text{POC}_{\text{fossil}}$  mobilization and the geomorphic processes responsible were assessed in the context of hydrometric measurements of suspended sediment concentration (SSC) and river stage height. Finally, the  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{14}\text{C}_{\text{org}}$  data from this Andean catchment shed new light on previous measurements of “old” ( $^{14}\text{C}$ -depleted) POC downstream in the Amazon Basin [Mayorga *et al.*, 2005].

## 2. Study Area

[6] The study area is located in the Eastern Cordillera of the Central Andes (Figure 1a), subject to rock and surface uplift of  $0.2\text{--}0.3\text{ mm yr}^{-1}$  due to the subduction of the Nasca Plate under the South American Plate [Gregory-Wodzicki, 2000]. Convergence has built steep topography [Montgomery *et al.*, 2001] whose juxtaposition with the South American Low Level Jet, which carries humid winds westward over the Amazon Basin [Marengo *et al.*, 2004], drives high annual precipitation on the eastern flank of the Andes of between 1250 mm to  $>7000\text{ mm}$  [Killeen *et al.*, 2007]. The climate and tectonics combine to drive moderate denudation rates, estimated from  $^{10}\text{Be}$  in detrital quartz, of  $\sim 0.4\text{ mm yr}^{-1}$  in the Central Andes [Wittmann *et al.*, 2009]. The steep slopes are prone to bedrock landslides, which contribute importantly to sediment transfer [Blodgett and Isacks, 2007]. In this part of the Andes, mountain rivers



**Table 1.** Catchment Descriptions

Gauge Station	Acronym	Latitude (°S)	Longitude (°W)	Area (km <sup>2</sup> )	Mean Basin Elevation (masl)	Minimum Basin Elevation (masl)	Maximum Basin Elevation (masl)	Meta-sedimentary (%)	Granite/High Grade Mafic (%)	Mean Slope (°)
San Pedro	SP	13°3'27"	71°32'40"	161	2810	1360	4000	79	21	26
Wayqecha	WQ	13°9'46"	71°35'21"	50	3180	2250	3910	100	0	28

drain large areas of sedimentary and meta-sedimentary melanges which run parallel to the range (Figure 1a), known to contain POC<sub>fossil</sub> [Bouchez *et al.*, 2010].

[7] Here we focus on the Kosñipata River in the Andes at two sites, the San Pedro catchment (1360 masl, 160 km<sup>2</sup>) and the Wayqecha sub-basin (2250 masl, 50 km<sup>2</sup>) (Figure 1b), whose bedrock geology is representative of a large Andean region (Figure 1a) and has not been extensively sampled by previous work [Hedges *et al.*, 2000; Mayorga *et al.*, 2005; Aufdenkampe *et al.*, 2007; Townsend-Small *et al.*, 2008]. The basins are dominantly underlain by Paleozoic (~450 Ma) meta-sedimentary mudstones (~80%), with plutonic intrusions contributing ~20% of the total San Pedro basin (Table 1) [Carlotto *et al.*, 1996]. Their geomorphic characteristics are typical of mountain river catchments, with the mean slope, derived from Shuttle Radar Topography Mission (SRTM) (90 × 90 m), of 28° in the San Pedro catchment and 26° in the Wayqecha sub-basin.

[8] The wet climate sustains productive tropical montane cloud forest on the steep hillslopes of the San Pedro catchment [Malhi *et al.*, 2010], located in Manu National Park where logging is prohibited. The forest contains significant stores of POC<sub>non-fossil</sub> in biomass and soil, with total carbon stocks ranging from 114 to 151 MgC ha<sup>-1</sup> [Girardin *et al.*, 2010], similar to those estimated for tropical forests worldwide [Dixon *et al.*, 1994] and representative of a wider geographical area in the Andean mountains [Malhi *et al.*, 2010]. Total carbon stocks do not vary greatly with elevation, with reduced standing biomass at high elevation offset by increased soil carbon stocks [Gibbon *et al.*, 2010; Girardin *et al.*, 2010; Zimmermann *et al.*, 2010].

### 3. Materials and Methods

#### 3.1. Sample Collection and Hydrometric Measurements

[9] At the San Pedro and Wayqecha catchment outlets, suspended sediment samples were collected in

the 2010 wet season. Samples were collected at high temporal resolution (three-hourly) at both sites continuously over 2 weeks which featured several flood events. We targeted flood events because: (i) the composition of POC can vary widely on short time scales [e.g., Hilton *et al.*, 2008b; Smith *et al.*, 2013], allowing us to better constrain the composition range of Andean POC; and (ii) to ensure our samples were collected at times when water, sediment, and POC transfer are thought to be volumetrically important in mountain rivers [Hilton *et al.*, 2008b; Kao and Milliman, 2008]. At both sample sites, large-scale bed roughness should lead to high turbulence and mixing in the channel, meaning our samples are likely to be representative of the suspended load [Lupker *et al.*, 2011]. Collections were made from the surface of the turbulent flow in plastic 250–500 mL Nalgene™ bottles pre-rinsed with filtered river water, using a sampling pole to reach the middle of the channel. A known volume of river water was filtered through 0.7 μm glass fiber filters (Whatman GF/F, 47 mm) to recover suspended sediment. Filters were dried at ~40°C within 1 day and stored in sterile petri dishes.

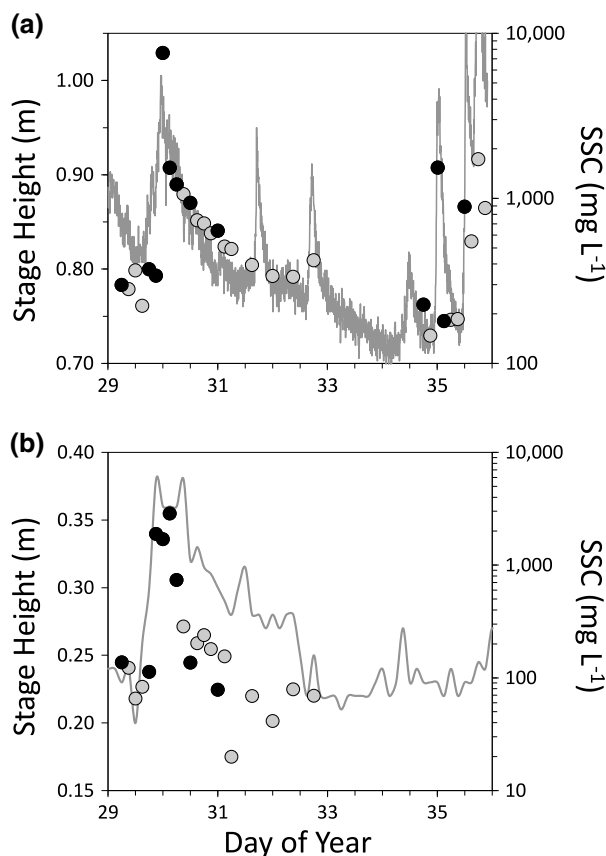
[10] To provide constraint on the elemental and isotopic composition of POC<sub>fossil</sub>, river bed materials were collected at low flow, during the dry season in July 2009 and again at high flow during the 2010 wet season [e.g., Galy *et al.*, 2007a, 2008b; Hilton *et al.*, 2010]. Approximately 500 g of sand and finer material were collected from active channel deposits. All riverbed material (n = 7) was dried <60°C within 1 week of collection and stored in sterile sample bags until analysis.

[11] To provide hydrodynamic context to the samples, hydrometric gauging stations were installed to monitor river stage height (m) at the San Pedro and Wayqecha catchment outlets (Figure 1b). At the San Pedro gauge, depth was measured 1.5 m from the river bank (total width 17 m), by a logger (WL16 Data Logger, Global Water Instrumentation, Inc), every 5 min. At the Wayqecha gauge, depth was measured with a rule from the same spot ~1 m from the river bank (total width 10 m) at discrete intervals upon river sample collection.

### 3.2. Geochemical Analyses

[12] Suspended sediment samples collected on the rising limb, storm peak, and falling limb of two storms were selected ( $n=52$ ) for analysis from the San Pedro and Wayqecha gauging stations (Figure 2). River suspended sediments were rinsed from the glass filter membrane using deionized water in glass beakers and the samples dried at 40°C. Pre-combusted quartz powder (with no measurable POC) was subjected to the same procedure to quantify procedural blanks. The sediment mass (mg) and known filtered volume (L) was used to calculate the suspended sediment concentration (SSC,  $\text{mg L}^{-1}$ ). One large suspended sediment sample from the San Pedro outlet (04 February 2010 at 0 h) was wet sieved into clay and silt ( $<63 \mu\text{m}$ ), sand ( $63\text{--}500 \mu\text{m}$ ), and coarse sand ( $>500 \mu\text{m}$ ) fractions. All riverbed materials ( $n=7$ ) were sieved to the  $63\text{--}250 \mu\text{m}$  size fractions to collect a sample of lithological sources [e.g., Galy *et al.*, 2008b; Bouchez *et al.*, 2010; Hilton *et al.*, 2010]. All samples were homogenized using a mortar and pestle. Inorganic carbon was removed using a 5 M HCl leach for 4 h at 75°C to remove all detrital carbonates (including dolomite) [Galy *et al.*, 2007a; Hilton *et al.*, 2008a; 2010], thus the following analyses refer to acid-insoluble POC. The HCl leach method has been shown to be the most robust way to return reliable organic carbon to nitrogen ratios in similar materials to those analyzed here [Brodie *et al.*, 2011]. Following deionized water rinses, samples were dried at 75°C and decanted to clean glass vials.

[13] An aliquot of each sediment sample was analyzed to determine their weight percent organic carbon ( $C_{\text{org}}$ , %) and nitrogen (N, %) using a Costech CHN elemental analyser (EA) by normalizing to an average of standards and corrected for an internal blank and procedural blank [Hilton *et al.*, 2010; Gröcke *et al.*, 2011]. Stable isotopes of POC ( $\delta^{13}C_{\text{org}}$ , ‰) were determined by continuous flow from the EA coupled via CONFLO-III to a Thermo-Delta-V isotope ratio mass spectrometer in the Stable Isotope Biogeochemistry Laboratory, University of Durham. Values were normalized based on measured values of IAEA and laboratory standards, corrected for any internal blank and procedural blank and reported in  $\delta^{13}C$  notation relative to VPDB. The precision ( $2\sigma$ ) and accuracy of  $\delta^{13}C_{\text{org}}$  were determined using standards measured under the same analytical conditions and were 0.1‰ [Gröcke *et al.*, 2011]. Replicates of suspended sediment of similar sediment matrix ( $n=42$ ) returned an average  $2\sigma$  of  $\pm 0.2\text{‰}$  and we take this as the average precision of the analyses.



**Figure 2.** River stage height (grey line, m) over the study period for (a) San Pedro (161 km<sup>2</sup> watershed area), and (b) Wayqecha (50 km<sup>2</sup> watershed area) gauging stations (Figure 1b). Samples for geochemical analysis shown as circles with suspended sediment concentration (SSC,  $\text{mg L}^{-1}$ ), where dark fill indicates the sample was also analyzed for <sup>14</sup>C content.

[14] A set of suspended sediment samples ( $n=21$ ) were prepared to graphite at the NERC Radiocarbon Facility, following inorganic carbon removal by acidification described previously, quantitative recovery of carbon in sealed quartz tubes followed by cryogenic separation of CO<sub>2</sub> [Boutton *et al.*, 1983]. Between 1 and 2 mg C was combusted for each sample, and standard and CO<sub>2</sub> was converted to an iron/graphite mix by iron/zinc reduction [Slota *et al.*, 1987] for <sup>14</sup>C measurement by AMS in the +1 charge state at 245 keV. The <sup>14</sup>C enrichment of POC in each sample was calculated as  $\Delta^{14}C_{\text{org}}$  as the relative difference between absolute international standard (relative to the year of measurement, 2011) and sample activity corrected for age and corrected to  $-25\text{‰}$   $\delta^{13}C_{\text{VPDB}}$  based on measured  $\delta^{13}C_{\text{org}}$  [Stuiver and Polach, 1977]. The fraction modern ( $F_{\text{mod}}$ ) is also reported where  $F_{\text{mod}} = (\Delta^{14}C_{\text{org}} + 1000)/992.648$  based on the correction factor for measurement in

2011. Overall average analytical precision at  $2\sigma$  was  $\Delta^{14}\text{C} = 3.20 \pm 0.55\%$ . Process standards (96H humin) and background materials (bituminous coal) were taken through all stages of sample preparation and  $^{14}\text{C}$  analysis and were within  $2\sigma$  uncertainty of expected values. The procedural quartz powder blank for the filtration stage contributed  $2 \times 10^{-4}$  mgC, which is 0.01% of the  $\text{CO}_2$  used for each  $^{14}\text{C}$  analysis, meaning that contamination from GF/F filters was negligible within the uncertainty on the analysis. The inorganic carbon removal procedure did not alter the  $\text{C}_{\text{org}}$ ,  $\delta^{13}\text{C}$  or  $\Delta^{14}\text{C}_{\text{org}}$  of standards subject to the procedure [Hilton *et al.*, 2008b].

## 4. Results

### 4.1. Suspended Load and River Stage Height

[15] At the San Pedro gauging station, the mean suspended sediment concentration (SSC,  $\text{mg L}^{-1}$ ) ranged from  $147 \text{ mg L}^{-1}$  to  $7594 \text{ mg L}^{-1}$ , with a mean  $\text{SSC} = 835 \pm 476 \text{ mg L}^{-1}$  ( $n=31$ ,  $\pm 2$  times standard error on the mean, given throughout the manuscript unless otherwise stated; Figure 2a). At the Wayqecha gauging station, the mean SSC was  $441 \pm 330 \text{ mg L}^{-1}$  ( $n=21$ ) and ranged from  $20 \text{ mg L}^{-1}$  to  $2869 \text{ mg L}^{-1}$  (Figure 2b). SSC was generally positively correlated with stage height, a surrogate for water discharge, in both catchments. The range of SSC values and this correlation were similar to other mountain rivers worldwide [Milliman and Syvitski, 1992]. Townsend-Small *et al.* [2008] captured storm events with SSC  $1800 \text{ mg L}^{-1}$  at Chorobama River at Oxapampa, Peru, and thus, the new data set represents the highest turbidity samples analyzed for POC from Andean headwaters.

[16] Over the study period, stage height at the San Pedro gauge (Figure 2a) ranged from 0.63 m to 1.18 m, with a mean of  $0.80 \pm 0.003$  m ( $n=4405$ ). At the Wayqecha gauge (Figure 2b), stage height ranged from 0.19 to 0.38 m, with a mean of  $0.25 \pm 0.01$  m ( $n=111$ ). These values can be compared to measurements taken over an entire year at San Pedro (from November 2009 to January 2011) to examine the relative magnitude of events captured during the sampling campaign. The annual mean stage height at San Pedro was  $0.50 \pm 0.003$  m ( $n=36,117$ ), with a range from 0.08 m to 2.71 m. Exceedance probability was determined from the mean river height for the San Pedro station at 6h intervals ( $n=761$ ) over the year record. Samples for POC were collected over a

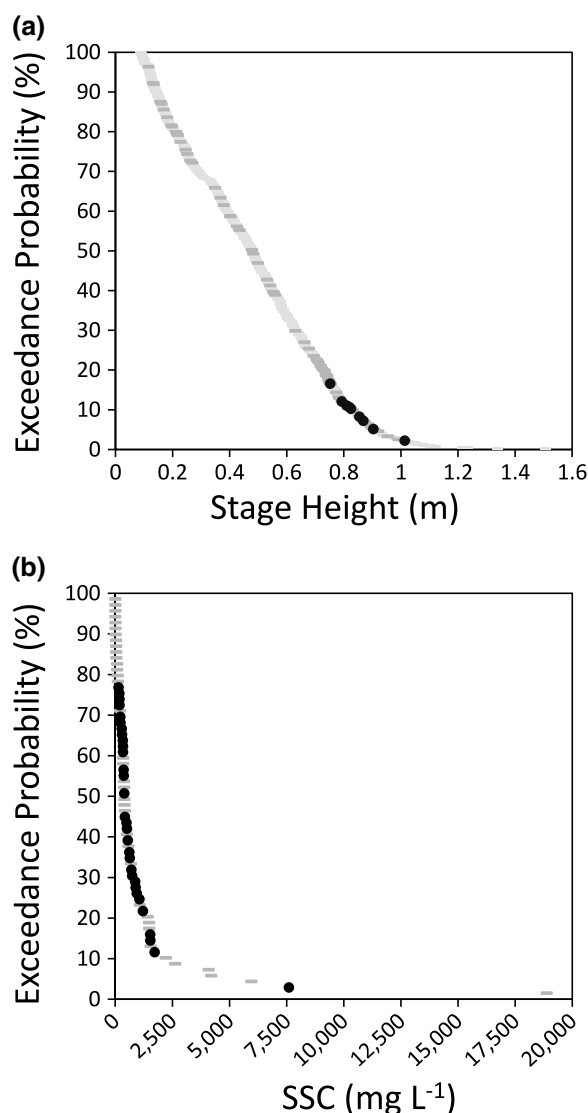
large range of flows (Figure 3a) and include two large events with an exceedance probability of 5.1% and 2.2%. The sampling period here (Figure 2a) therefore captured times of high turbidity (Figure 3b) and high stage height (Figure 3a) which reflect periods when most of the suspended load mass transfer is likely to occur in mountain catchments [Hilton *et al.*, 2008b; Kao and Milliman, 2008]. While our samples cover a representative range of flow conditions (Figure 3), in the absence of water discharge, we have not averaged geochemical measurements by flux. Instead, we focus on discussions of the range in compositional variability as a means to better characterize Andean POC.

### 4.2. Elemental Geochemistry

[17] The mean  $\text{C}_{\text{org}}$  of suspended load samples from the Kosñipata Valley over the sampling period was  $0.92 \pm 0.24\%$  ( $n=54$ ), with a slightly higher mean at San Pedro ( $0.96 \pm 0.39\%$ ,  $n=33$ ) than Wayqecha ( $0.86 \pm 0.10\%$ ,  $n=21$ ) (see Table S1, supporting information).<sup>1</sup> The  $\text{C}_{\text{org}}$  values were at the lower end of the range reported from other Andean-sourced catchments [Aufdenkampe *et al.*, 2007; Townsend-Small *et al.*, 2008] but slightly higher than measured POC in the Beni River of between 0.47% and 0.61% [Bouchez *et al.*, 2010]. Riverbed materials had a lower mean  $\text{C}_{\text{org}} = 0.36 \pm 0.03\%$  ( $n=7$ ), which was similar to the  $\text{POC}_{\text{fossil}}$  content of Andean rocks of  $0.3 \pm 0.1\%$  inferred from measurements on the Beni River [Bouchez *et al.*, 2010], thus consistent with a dominant origin of the river bed material from  $\text{POC}_{\text{fossil}}$  [Hilton *et al.*, 2010].

[18]  $\text{C}_{\text{org}}$  displayed a positive relationship with N ( $\text{C}_{\text{org}} = 6.5 \pm 0.8 \times \text{N} - 0.15 \pm 0.12$ ,  $n=51$ ,  $r^2=0.6$ ,  $P<0.0001$ ), and the negative intercept within error of zero suggests the majority of N in the samples is associated with POC, meaning the nitrogen to organic carbon ratio (N/C) can record organic matter source [e.g., Goni *et al.*, 2008; Hilton *et al.*, 2010]. The mean N/C of the suspended load samples was  $0.18 \pm 0.01$  ( $n=54$ ) and ranged from 0.03 to 0.25, with the same mean at San Pedro ( $0.18 \pm 0.02$ ,  $n=33$ ) as at Wayqecha ( $0.17 \pm 0.01$ ,  $n=21$ ). These values were lower than the mean of river bed materials,  $\text{N/C} = 0.29 \pm 0.03$  ( $n=7$ ), but higher than N/C measured in soil ( $\text{O}_\text{H}$  and A layers) and vegetation in the valley, with N/C values of  $0.06 \pm 0.01$  ( $n=4$ )

<sup>1</sup>All supporting information may be found in the online version of this article.



**Figure 3.** Exceedance probability (%) for hydrometric measurements from the Kosñipata River. (a) Mean river height (6 h) over the longer-term study period as light grey dashes, with suspended sediment samples from the year-long study as dark grey dashes, and with suspended sediment samples from this study as black circles. (b) Suspended sediment concentration (mg L<sup>-1</sup>) of samples collected over the year-long study as grey dashes and samples from this study as black circles.

and  $0.05 \pm 0.01$  ( $n=66$ ), respectively [Zimmermann *et al.*, 2009; Rao, 2011].

### 4.3. Isotope Geochemistry

[19] The mean  $\delta^{13}\text{C}_{\text{org}}$  of suspended POC in the Kosñipata River was  $-25.7 \pm 0.4\text{‰}$  ( $n=54$ ) and ranged  $\sim 9\text{‰}$  from  $-20.9\text{‰}$  to  $-30.3\text{‰}$ . Mean  $\delta^{13}\text{C}_{\text{org}}$  values were similar at San Pedro and Wayqecha, of  $-25.6 \pm 0.5\text{‰}$  and  $-25.8 \pm 0.5\text{‰}$ , respectively. The  $\delta^{13}\text{C}_{\text{org}}$  values were consistent with

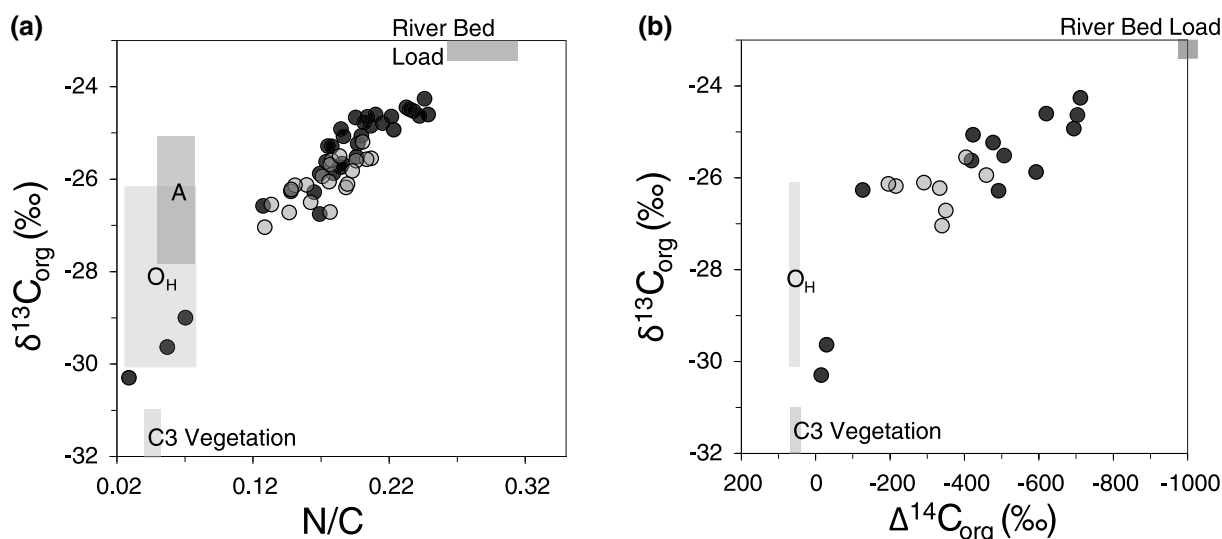
riverine POC measured elsewhere in the Andes [Hedges *et al.*, 2000; Mayorga *et al.*, 2005; Townsend-Small *et al.*, 2005; Aufdenkampe *et al.*, 2007; Townsend-Small *et al.*, 2008], but were mostly higher than those expected of C3 vegetation in mountain forests [Körner *et al.*, 1988]. Published values from tropical montane cloud forests in the Andes have C3 vegetation with  $\delta^{13}\text{C}_{\text{org}}$  between  $-31.1\text{‰}$  and  $-28.2\text{‰}$ , [Hietz *et al.*, 2002; Townsend-Small *et al.*, 2005], consistent with measurements from the Kosñipata Valley [Rao, 2011]. Soil profiles in the valley had higher  $\delta^{13}\text{C}_{\text{org}}$  values compared to C3 vegetation but were still lower than the majority of riverine POC, with the O<sub>H</sub> layer with a mean of  $-28.1 \pm 2.0\text{‰}$  ( $n=2$ ) and A layers with a mean of  $-26.5 \pm 1.4\text{‰}$  ( $n=2$ ) [Zimmermann *et al.*, 2009]. In contrast, the riverbed materials had a higher  $\delta^{13}\text{C}_{\text{org}}$  than the suspended load, surface vegetation, and soil, with a mean  $-23.2 \pm 0.2\text{‰}$  ( $n=7$ ), similar to that measured in meta-sedimentary bedrocks elsewhere [Galy *et al.*, 2008b; Hilton *et al.*, 2010].

[20] The mean  $\Delta^{14}\text{C}_{\text{org}}$  of the selected samples was  $-400 \pm 90\text{‰}$  ( $n=21$ ) and ranged from  $-712\text{‰}$  to  $-15\text{‰}$  over the sampling period (Table S1). The mean  $\Delta^{14}\text{C}_{\text{org}}$  at San Pedro was lower ( $-447 \pm 136\text{‰}$ ,  $n=13$ ) than at Wayqecha ( $-324 \pm 63\text{‰}$ ,  $n=8$ ). These values were generally lower than those measured at low SSC from other Andean catchments [Mayorga *et al.*, 2005; Aufdenkampe *et al.*, 2007; Townsend-Small *et al.*, 2007] but consistent with the range reported in the Beni River at Rurrenabaque during high flow, from  $-449\text{‰}$  to  $-590\text{‰}$  [Bouchez *et al.*, 2010]. The low  $\Delta^{14}\text{C}_{\text{org}}$  values of POC mirror those from mountain rivers elsewhere which erode radiocarbon-dead ( $\Delta^{14}\text{C}_{\text{org}} = -1000\text{‰}$ ) POC<sub>fossil</sub> from sedimentary bedrock [Kao and Liu, 1996; Komada *et al.*, 2004; Leithold *et al.*, 2006; Hilton *et al.*, 2008b].

### 4.4. Evidence for Mixing of POC Sources

[21] The  $\delta^{13}\text{C}_{\text{org}}$  values of the suspended load were positively correlated with the N/C ratio ( $r^2=0.73$ ,  $P<0.0001$ ,  $n=54$ ; Figure 4a). A linear relationship between the stable carbon isotopic composition and the inverse of  $\text{C}_{\text{org}}$  concentration can be produced by biogeochemical processing which fractionates  $\delta^{13}\text{C}_{\text{org}}$  while  $\text{C}_{\text{org}}$  varies, or it can result from a binary mixture of two end-members with distinct compositions. The latter is common in river systems with rapid throughput of particulate materials [e.g., Hilton *et al.*, 2008a; 2010], and the former mainly observed within soil profiles [e.g., Baisden *et al.*, 2002; Zimmermann *et al.*, 2009]. The linear





**Figure 4.** Elemental and isotopic composition of POC in suspended load (circles) from the Kosñipata River. Samples collected from San Pedro as black circles and from Wayqecha as grey circles, with analytical uncertainties smaller than the point size. (a) The stable isotopes of POC ( $\delta^{13}\text{C}_{\text{org}}$ , ‰) versus the nitrogen to organic ratio (N/C), (b)  $\delta^{13}\text{C}_{\text{org}}$  (‰) versus the radiocarbon content ( $\Delta^{14}\text{C}_{\text{org}}$ , ‰). For display, river materials plotted at the radiocarbon depleted end member ( $\Delta^{14}\text{C}_{\text{org}} = -1000$ ‰ see main text for discussion). Boxes show ranges from published sources [Zimmermann *et al.*, 2009; Rao, 2011], where  $\text{O}_\text{H}$  and A are soil horizons.

trend intercepted the measured  $\delta^{13}\text{C}_{\text{org}}$  and N/C values of river bed materials, and trended toward those of C3 vegetation and soils at low N/C (Figure 4a), suggesting that a mixing process is setting the compositional range of the variables.

[22] These trends were mirrored by a negative correlation between  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{14}\text{C}_{\text{org}}$  in the suspended load ( $r^2 = 0.67$ ,  $P < 0.0001$ ,  $n = 21$ ; Figure 4b). A linear correlation between isotopic measurements of the same element can be indicative of mixing, and the trend ( $\delta^{13}\text{C}_{\text{org}} = -0.006 \pm 0.001 \times \Delta^{14}\text{C}_{\text{org}} + 28.5 \pm 0.4$ ) intercepts the measured  $\delta^{13}\text{C}_{\text{org}}$  of riverbed materials at  $\Delta^{14}\text{C}_{\text{org}} = -1000$ ‰ and the  $\delta^{13}\text{C}_{\text{org}}$  values of plant and soils in the valley at high  $\Delta^{14}\text{C}_{\text{org}}$ . Both correlations (Figure 4) suggest that mixing between  $\text{POC}_{\text{fossil}}$  (represented by riverbed materials) and  $\text{POC}_{\text{non-fossil}}$  sources plays the dominant role in controlling the N/C,  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{14}\text{C}_{\text{org}}$  values of the suspended load, analogous to the binary mixing of POC sources observed in small mountain rivers draining sedimentary bedrock throughout the world [Kao and Liu, 2000; Komada *et al.*, 2004; Leithold *et al.*, 2006; Hilton *et al.*, 2008b; 2010].

## 5. Discussion

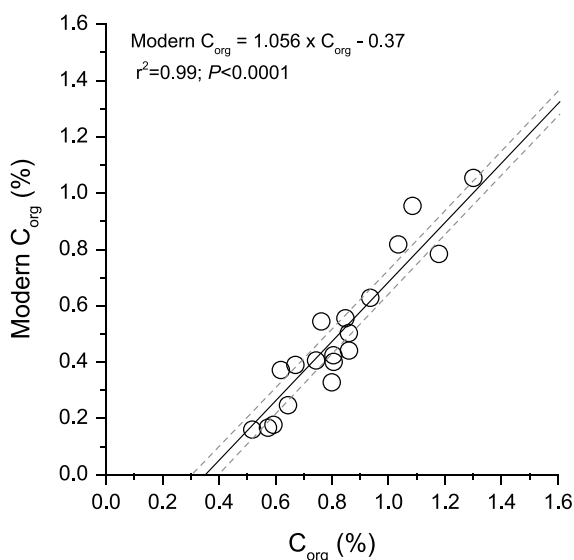
### 5.1. Source of Andean POC

[23] Constraining the source of POC carried by rivers is fundamental to understanding how the erosion,

transfer, processing, and/or deposition of POC impacts the carbon cycle and how these carbon transfers might be moderated by changing climate. The erosion and transfer of  $\text{POC}_{\text{non-fossil}}$  represent an export of primary productivity [Hilton *et al.*, 2008b; 2012], which if escapes oxidation during transport [Mayorga *et al.*, 2005; Cole *et al.*, 2007; Tranvik *et al.*, 2009] and is buried in long-term sedimentary deposits would result in a sink of atmospheric  $\text{CO}_2$  [Galy *et al.*, 2007a]. In contrast, erosion in mountain belts underlain by sedimentary bedrock can mobilize  $\text{POC}_{\text{fossil}}$  [Blair *et al.*, 2003; Hilton *et al.*, 2011a; Graz *et al.*, 2012].  $\text{POC}_{\text{fossil}}$  input can play an important role in setting the elemental and isotopic composition of riverine POC [Komada *et al.*, 2004; Hilton *et al.*, 2010], while its oxidation counters the  $\text{CO}_2$  drawdown caused by  $\text{POC}_{\text{non-fossil}}$  burial [Copard *et al.*, 2007; Bouchez *et al.*, 2010; Hilton *et al.*, 2011a]. Here we examine the composition of POC in this Andean river to better constrain the input of these components.

[24] Various approaches have been used to quantify the  $\text{POC}_{\text{fossil}}$  contribution to river suspended load. Radiocarbon presents an ideal tracer if there is organic carbon input from relatively young sources (e.g.,  $\Delta^{14}\text{C}_{\text{org}} > -100$ ‰) and aged soils are not prevalent [Gomez *et al.*, 2010], which is often the case in mountain catchments [Hilton *et al.*, 2008b]. Due to the 5730 year half-life of  $^{14}\text{C}$  [Godwin, 1962], one can assume that the carbon derived from bedrock, termed  $\text{POC}_{\text{fossil}}$ , is indistinguishable from background (i.e., radiocarbon dead) [Galy *et al.*, 2007b;





**Figure 5.** Organic carbon concentration ( $C_{org}$  %) versus modern  $C_{org}$  % ( $C_{org} \% \times \text{Fraction Modern}, F_{mod}$ ) for San Pedro and Wayqecha River POC samples for a single hydrological event. Linear fit is the solid line and 95% confidence intervals as dashed lines, ( $r^2=0.99$ ,  $P < 0.0001$ ,  $n = 16$ ).

Hilton *et al.*, 2008b] and with knowledge of the  $\Delta^{14}C_{org}$  content of soils and vegetation, the fraction of  $POC_{fossil}$  ( $F_f$ ) and assuming that these are the predominant two carbon sources can be determined following two component mixing theory:

$$\Delta^{14}C_x = F_{nf} \times \Delta^{14}C_{nf} + F_f \times \Delta^{14}C_f \quad (1)$$

where  $\Delta^{14}C_x$  is the  $\Delta^{14}C_{org}$  of the measured POC sample,  $\Delta^{14}C_{nf}$  and  $\Delta^{14}C_f$  are the  $\Delta^{14}C_{org}$  values of the  $POC_{non-fossil}$  end-member and  $POC_{fossil}$  end-member, respectively. The mass fraction of  $POC_{non-fossil}$  and  $POC_{fossil}$  to the total POC content are  $F_{nf}$  and  $F_f$ , respectively. Thus, by definition,  $F_{nf} + F_f = 1$  for a binary mixture, and so

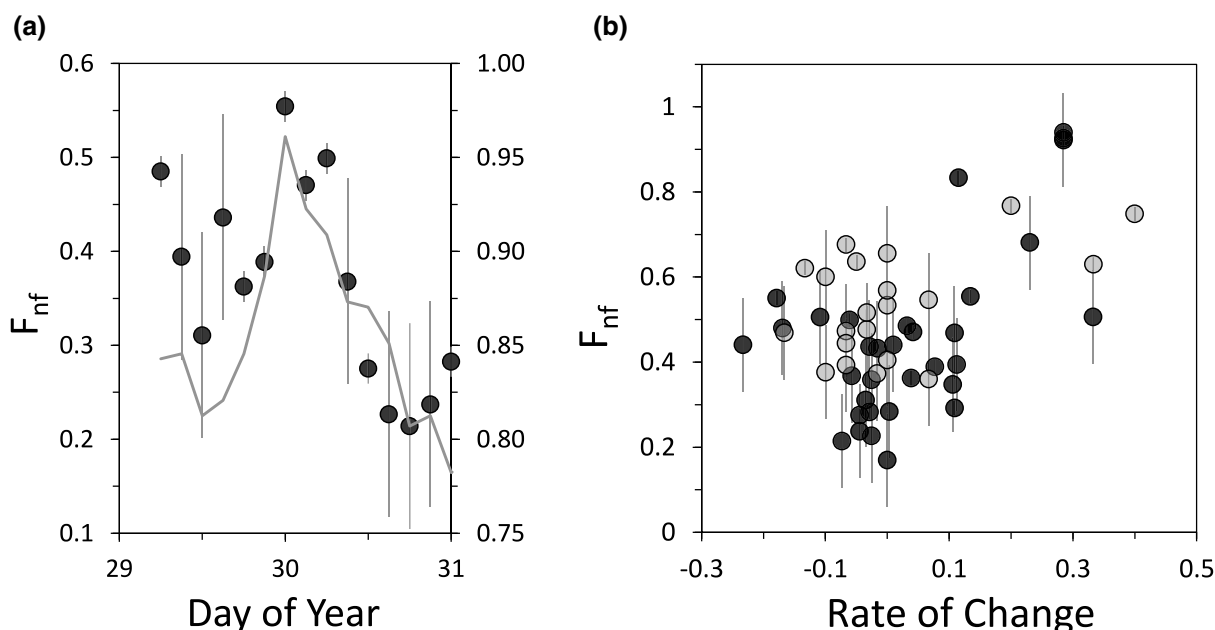
$$F_f = \frac{\Delta^{14}C_x - \Delta^{14}C_{nf}}{\Delta^{14}C_f - \Delta^{14}C_{nf}} \quad (2)$$

[25] To constrain the  $\Delta^{14}C_{nf}$  (equation (2)) eroded from the catchment, we can apply the technique of Galy *et al.* [2008a] assuming the rivers carry a well-mixed sample of POC sources (Figure 4) and plotting  $C_{org}$  versus the  $C_{org}$  multiplied by the fraction modern ( $F_{mod}$ ) from radiocarbon (Figure 5). This approach is analogous to the “standard addition” method, if we start with a sample with only  $POC_{fossil}$  (i.e.,  $C_{org} \times F_{mod} = 0$ ) adding  $POC_{non-fossil}$  in increments, this will increase  $C_{org}$  and  $F_{mod}$ . If the system is mixed, the intercept of the linear trend informs us

of the average  $C_{org}$  of  $POC_{fossil}$  [Galy *et al.*, 2008a; Bouchez *et al.*, 2010], while the gradient reflects the average  $F_{mod}$  of  $POC_{non-fossil}$ , i.e., average age of carbon sources from recently photosynthesized material [Galy and Eglinton, 2011]. For the samples from the first storm in the Kosñipata River ( $n = 16$ ; Figure 2), the linear trend (Figure 5) suggests an average  $POC_{fossil}$  content of  $0.37 \pm 0.03\%$ , consistent with the measured  $C_{org}$  from river bed materials (mean  $C_{org} = 0.36 \pm 0.03\%$ ) thought to be dominated by  $POC_{fossil}$ . The average  $F_{mod}$  of the eroded biosphere of  $1.056 \pm 0.015$  is consistent with extrapolated atmospheric  $^{14}C$  values around the time of sampling [Hua and Barbetti, 2004] and measurements from Andean soils [Townsend-Small *et al.*, 2007]. The data suggest a young age of  $POC_{non-fossil}$ , which is to be expected given the high rates of physical erosion and surface turnover in mountain catchments [Hilton *et al.*, 2012].

[26] To determine the  $F_f$  (and  $F_{nf}$ ) for each sample with  $^{14}C$  analyses, we set  $\Delta^{14}C_f = -1000\text{‰}$  (radio-carbon dead) and  $\Delta^{14}C_{nf}$  to the linear gradient of the “standard addition” method (Figure 5) of  $F_{mod} = 1.056 \pm 0.015$ , equivalent to  $\Delta^{14}C_{org} = 48 \pm 15\text{‰}$ . The propagated uncertainty of the end members suggests  $F_f$  (and  $F_{nf}$ ) can be quantified to within 0.02 on average using  $\Delta^{14}C_{org}$ . The linear trend between N/C and  $\delta^{13}C_{org}$  (Figure 4) suggests these variables can also be used to quantify  $F_{nf}$  in the absence of  $\Delta^{14}C_{org}$ . This is beneficial, since it extends the assessment to the larger sample set [e.g., Hilton *et al.*, 2010]. Here we use the N/C, since the N/C of  $POC_{non-fossil}$  sources appears relatively constant in comparison to  $\delta^{13}C_{org}$  (Figure 4a) [Zimmermann *et al.*, 2009; Rao, 2011]. Using the measured N/C of riverbed materials as the  $POC_{fossil}$  composition (N/C =  $0.29 \pm 0.03$ ) and the published N/C of vegetation and soil (N/C =  $0.05 \pm 0.02$ ) [Zimmermann *et al.*, 2009; Rao, 2011], we adapt equation (2) to quantify  $F_{nf}$  using N/C ( $F_{nf:N/C}$ ). The absolute uncertainty on  $F_{nf:N/C}$  based on the end-member values ranges from 0.08 to 0.14, with an average of 0.1, which is 6–10 times lower than the range of  $F_{nf}$  values. A plot of  $F_{nf}$  from  $\Delta^{14}C_{org}$  versus  $F_{nf:N/C}$  has a significant linear relationship ( $P < 0.0001$ ) with a gradient of  $1.0 \pm 0.1$  and intercept within error of zero ( $-0.05 \pm 0.09$ ). Therefore,  $F_{nf:N/C}$  provides a robust quantification of  $POC_{fossil}$  input.

[27] The results of this mixing analysis demonstrate the significant input of  $POC_{fossil}$  to the river load of these catchments, with an average  $F_{nf}$  of  $0.49 \pm 0.05$  ( $n = 54$ ), ranging between  $0.17 \pm 0.05$  and  $0.94 \pm 0.09$ . These values indicate that up to ~80% of the POC carried by this river throughout this period was derived from sedimentary bedrock,



**Figure 6.** (a) The fraction non-fossil POC ( $F_{nf}$ ) during flood events plotted as circles, with river stage height (m) shown as grey line. The first storm sampled over the study period is shown for San Pedro and other sampled events (Figure 2) show a similar pattern. (b)  $F_{nf}$  versus rate of change of river height over the 6 h preceding sample collection, with samples from San Pedro as black circles and Wayqecha as grey circles. Positive rate of change indicates the rising limb of flood hydrographs and negative rate of change shows the falling limb. In all parts, whiskers show errors on  $F_{nf}$  values.

with a range between 6% and 80%. Even when  $F_f$  is low,  $\text{POC}_{\text{fossil}}$  contributes the same fraction of mass to the suspended sediment, demonstrated by the constant weight % of  $\text{POC}_{\text{fossil}}$  ( $0.37 \pm 0.03\%$ ) observed in the suspended load (Figure 5). These values of  $F_{nf}$  are within the range measured in small mountain rivers elsewhere [Kao and Liu, 2000; Komada et al., 2004; Hilton et al., 2008b; Hilton et al., 2010]. However, they are the first which suggest that  $\text{POC}_{\text{fossil}}$  input to Andean headwaters is quantitatively important across a range of hydro-metric conditions important for sediment export (Figure 3). Given the prevalence of sedimentary bedrocks in Andean catchments of this region (Figure 1), it is likely that  $\text{POC}_{\text{fossil}}$  input is more widespread and may impact the composition of POC in the lowland Amazon Basin (see section 5.3).

## 5.2. Hydrologic and Geomorphic controls on POC source

[28] In the study of POC transfer in mountain rivers it has been challenging to constrain both the source of POC and the hydrological conditions under which POC is transported, with one or the other not measured [e.g., Lyons et al., 2002; Leithold et al., 2006; Hilton et al., 2008a]. Only with this combination can the processes by which POC is mobilized be better constrained [Kao and Liu,

2000; Hatten et al., 2012; Hilton et al., 2012], allowing us assess how and why POC delivery varies in space and time. Here we benefit from high frequency sampling of river loads during the rising limb, peak, and falling limb of flood events (Figure 2) and geochemical quantification of  $\text{POC}_{\text{fossil}}$  and  $\text{POC}_{\text{non-fossil}}$  inputs (Figure 4). This allows the hydrological and geomorphic controls on POC transfer to be assessed.

[29] The available data suggest that the source of POC is variable over the course of flood events in both catchments (Figure 6). The highest values of  $F_{nf}$  generally occur at the flood peak (Figure 6a), in accordance with findings from mountain rivers in Taiwan [Hilton et al., 2008b; 2012]. Additional constraint comes from examining different hydrological regimes, afforded by the high temporal resolution of our sampling method (Figures 2 and 3). During rising river stage,  $F_{nf}$  is generally higher than during the falling stage (Figure 6b). This observation is consistent with the erosion processes known to operate in mountain catchments. In these turbid rivers, aquatic productivity is minimal and is not a dominant source of POC (Figure 4a). Therefore  $\text{POC}_{\text{non-fossil}}$  must be mostly supplied from the steep forested hillslopes which are tightly coupled to incising river channels [Fuller et al., 2003]. Erosion by overland flow [Gomi et al., 2008] and in the absence of soil saturation fast

lateral flow through soil horizons can mobilize  $\text{POC}_{\text{non-fossil}}$  from soil and plant debris [Crespo *et al.*, 2011].

[30] Another source of  $\text{POC}_{\text{non-fossil}}$  during heavy rainfall is from mass wasting processes which supply soil and coarse woody debris [Hilton *et al.*, 2011b; West *et al.*, 2011] along with clastic sediment and  $\text{POC}_{\text{fossil}}$  to the river [Hovius *et al.*, 2000; Hilton *et al.*, 2011a]. Mechanical attrition of this coarse woody debris can add  $\text{POC}_{\text{non-fossil}}$  [cf. Attal and Lavé, 2009]. Both processes act to increase the supply of  $\text{POC}_{\text{non-fossil}}$  during heavy rainfall and thus the rising limb and peak of flood events (Figure 6) [Hilton *et al.*, 2012].

[31] To corroborate the inferred erosion processes responsible for  $\text{POC}_{\text{non-fossil}}$  delivery to the river channel, the origin of  $\text{POC}_{\text{non-fossil}}$  can be assessed using the  $\delta^{13}\text{C}_{\text{org}}$  which varies between standing biomass and partially degraded soil organic matter in the valley [Zimmermann *et al.*, 2009; Rao, 2011]. If we project the suspended load compositions at low N/C and high  $\Delta^{14}\text{C}_{\text{org}}$  (i.e., the  $\text{POC}_{\text{non-fossil}}$  end-member) we find that most of the samples suggest supply from the upper soil ( $\text{O}_\text{H}$ ) with  $\delta^{13}\text{C}_{\text{org}}$  approximately  $-26\text{‰}$  to  $-28\text{‰}$  (Figure 4). We also find that plant debris can be important at the peak of floods, with the second storm having  $\delta^{13}\text{C}_{\text{org}}$  values less than  $-29.5\text{‰}$  at low N/C and high  $\Delta^{14}\text{C}_{\text{org}}$  (Figure 4). These observations confirm the dual role of overland flow and mass wasting processes in supplying  $\text{POC}_{\text{non-fossil}}$  to mountain rivers.

[32] The hydrological controls on POC source are superimposed upon a difference in the proportion of  $\text{POC}_{\text{non-fossil}}$  and  $\text{POC}_{\text{fossil}}$  between the San Pedro and Wayqecha catchments (Figure 4). During the first sampled storm (Figure 2), mean  $F_{\text{nf}}$  was  $0.49 \pm 0.05$  ( $n=21$ ) at San Pedro and ranged from 0.17 to 0.55. In the Wayqecha sub-catchment,  $F_{\text{nf}}$  was higher (mean =  $0.54 \pm 0.05$ ,  $n=21$ ), with higher values at the extremes of the range from 0.36 to 0.77. These differences cannot be explained by an increased relative contribution of  $\text{POC}_{\text{non-fossil}}$  at Wayqecha, because the carbon stock in standing biomass and soil is approximately constant with elevation in this forest [Zimmermann *et al.*, 2009; Girardin *et al.*, 2010]. Instead, they are likely to reflect an increased relative contribution from  $\text{POC}_{\text{fossil}}$  at San Pedro.  $\text{POC}_{\text{fossil}}$  can be supplied to river channels by bedrock landslides [Hilton *et al.*, 2011b], debris flows and gully erosion [Leithold *et al.*, 2006]. In the San Pedro catchment, the mean slope is higher than the upstream area at Wayqecha. Due to the important control on mass wasting

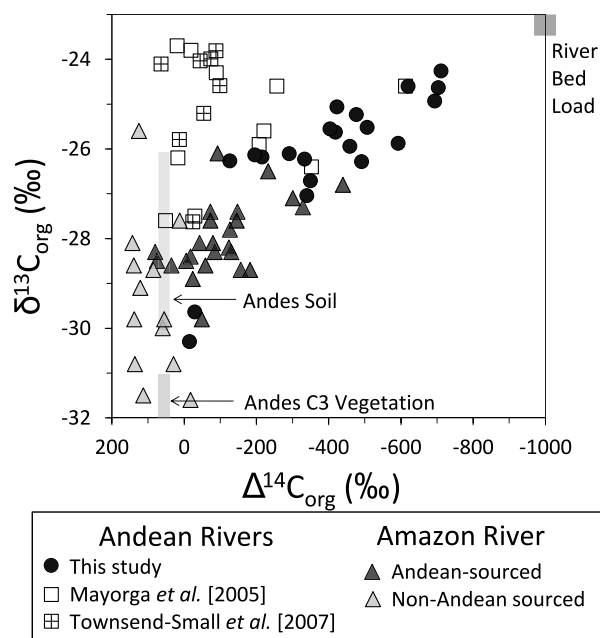
processes by slope angle [Dietrich *et al.*, 2003; Clarke and Burbank, 2010], one would expect a higher frequency of mass wasting events which can supply  $\text{POC}_{\text{fossil}}$  to channels across the San Pedro catchment area. This is consistent with the higher measured SSC in San Pedro (mean  $835 \text{ mg L}^{-1}$ ) compared to Wayqecha (mean  $441 \text{ mg L}^{-1}$ ), demonstrating enhanced input of clastic material which contains  $\text{POC}_{\text{fossil}}$  in this catchment.

### 5.3. Implications for Supply of Andean POC to the Amazon River

[33] In the major tributaries of the Amazon Basin, radiocarbon-depleted POC has been observed during high flow and at high SSC [Aufdenkampe *et al.*, 2007], with a number of  $\Delta^{14}\text{C}_{\text{org}}$  values less than  $-300\text{‰}$  [Mayorga *et al.*, 2005; Bouchez *et al.*, 2010]. This old POC is not present in samples collected from lowland rivers with no direct Andean inputs, whose  $\Delta^{14}\text{C}_{\text{org}}$  values are generally  $>0\text{‰}$  [Hedges *et al.*, 1986b; Mayorga *et al.*, 2005], leading to the hypothesis that the signature is derived from the Andes. However, while published measurements of Andean POC from the upper Beni River and upper Ucayali River show some radiocarbon depletion [Mayorga *et al.*, 2005; Townsend-Small *et al.*, 2007], the majority have  $\Delta^{14}\text{C}_{\text{org}}$  values greater than  $-200\text{‰}$  and have much higher  $\delta^{13}\text{C}_{\text{org}}$  values than observed in the lowland rivers. Therefore, the reasons behind the observed  $^{14}\text{C}$  depletion in the Amazon Basin remain uncertain. It may derive from an aging of POC [Mayorga *et al.*, 2005], implying that old soil POC exists in the tributaries sourced from the Andes, or from the input of  $\text{POC}_{\text{fossil}}$  eroded from sedimentary rocks [e.g., Galy *et al.*, 2008a; Hilton *et al.*, 2010]. These scenarios cannot be assessed without improved constraint on the isotopic composition of Andean POC.

[34] Existing Andean POC measurements are from samples collected toward the end of the dry season when river discharge and SSC were low. Low water stage samples may reflect compositions not prevalent during high runoff and SSC [Hilton *et al.*, 2008b; Hatten *et al.*, 2012], such as those influenced by aquatic productivity [Townsend-Small *et al.*, 2007]. In addition, some of the sampled Andean POC comes from glacial catchments above the tree line draining plutonic bedrocks (Figure 1a) [Mayorga *et al.*, 2005] which are not representative of the humid slopes of much of the Andes where tropical forest thrives [Gentry and Ortiz, 1993; Still *et al.*, 1999; Malhi *et al.*, 2010] and sedimentary bedrock is widespread (Figure 1a).





**Figure 7.** Stable isotopic composition ( $\delta^{13}\text{C}_{\text{org}}$ , ‰) and radiocarbon content ( $\Delta^{14}\text{C}_{\text{org}}$ , ‰) of POC for published data and those collected in this study. Andean headwater samples from high altitude sites collected at low turbidity from Mayorga *et al.* [2005] are shown as squares and from Townsend-Small *et al.* [2007] are shown as squares with crosses. All other samples were collected during the wet season, with Andean samples from the Kosñipata River in this study (black circles), Andean-sourced Amazon River samples (dark grey triangles), Amazon River tributaries with no Andean source (light grey triangles), with samples re-classified from Mayorga *et al.* [2005] based on their upstream contributing area.

The new constraint on Andean POC composition from the Kosñipata River, whose underlying bedrock geology and productive forest are representative of a larger area (Figure 1a), allows us to re-examine the existing measurements of  $\Delta^{14}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{org}}$  from the Amazon basin (Figure 4).

[35] When the published POC data from Andean-fed tributaries of the lowland Amazon River are examined alongside the new  $\Delta^{14}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{org}}$  measurements from the Andes, the vast majority describe a general linear trend which intersects the  $\delta^{13}\text{C}_{\text{org}}$  of Andean river bed materials ( $-23.2 \pm 0.2\text{‰}$ ) at low  $\Delta^{14}\text{C}_{\text{org}}$ , and soil and vegetation values at high  $\Delta^{14}\text{C}_{\text{org}}$  (Figure 7). In stark contrast, lowland rivers with no Andean river inputs (presumed to source POC from the floodplain) have a much higher  $\Delta^{14}\text{C}_{\text{org}}$  and a larger range in  $\delta^{13}\text{C}_{\text{org}}$ . We therefore propose that the observed old POC in the lowland Amazon Basin is derived from mixing

of radiocarbon-dead  $\text{POC}_{\text{fossil}}$  from the Andes (similar to the Kosñipata River) with young  $\text{POC}_{\text{non-fossil}}$  (Figure 7). Given that sedimentary rocks are prevalent in the Peruvian Andes draining to the Amazon, consisting of  $\sim 70\%$  of the total area (Figure 1a), the findings are consistent with other large basins fed by tectonically active mountain belts where  $\text{POC}_{\text{fossil}}$  is not completely oxidized [Galy *et al.*, 2007b; 2008a]. The explanation for the paired evolution of  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{14}\text{C}_{\text{org}}$  values in the lowland Amazon challenges an interpretation that the vast majority of Andean POC is mineralized within a short distance from the Andes during transport [Mayorga *et al.*, 2005]. Instead, the mixing hypothesis described here (Figure 7) suggests that  $\text{POC}_{\text{fossil}}$  may contribute between  $\sim 10\%$  and  $\sim 50\%$  of the POC carried in lowland rivers of the Amazon Basin (based on  $\Delta^{14}\text{C}_{\text{org}}$ ), but has not previously been considered as quantitatively important. In addition, the new data show that Andean  $\text{POC}_{\text{non-fossil}}$  eroded from tropical montane cloud forests can have similar isotopic composition as lowland forests, with a very low  $\delta^{13}\text{C}_{\text{org}}$  (approximately  $-30\text{‰}$ ) and high  $\Delta^{14}\text{C}_{\text{org}}$  (Figure 7). In light of the new data, the compositional range of the published POC data suggests less loss of Andean  $\text{POC}_{\text{non-fossil}}$  than is commonly asserted [Mayorga *et al.*, 2005]. Our data thus provide impetus to further investigate the role of Andean POC in the Amazon River. Here we have focused on characterization of POC source in turbid waters of small mountain catchments in the Kosñipata River. However, it would be beneficial to obtain further measurements from catchments draining  $\text{POC}_{\text{fossil}}$  [e.g., Bouchez *et al.*, 2010] to ascertain whether the isotopic and elemental compositions measured here are fully representative. While outside the scope of the current study, quantification of the fluxes of  $\text{POC}_{\text{non-fossil}}$  and  $\text{POC}_{\text{fossil}}$  (in  $\text{t km}^{-2} \text{yr}^{-1}$ ) exported from Andean catchments [e.g., Hilton *et al.*, 2011a, 2012] would also help re-assess the net contribution of POC from the mountainous headwaters (e.g., Figure 7).

## 6. Conclusions

[36] We measured the elemental (N/C) and stable carbon isotopic composition ( $\delta^{13}\text{C}_{\text{org}}$ ) and radiocarbon content ( $\Delta^{14}\text{C}_{\text{org}}$ ) of POC in an Andean mountain river draining sedimentary bedrock representative of a larger region. The data from turbid flood events (SSC up to  $7,600 \text{ mg L}^{-1}$ ) provide new insight on the composition and source of Andean POC at times when the majority of particulate materials are exported. N/C,  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{14}\text{C}_{\text{org}}$

distinguish between very young ( $\Delta^{14}\text{C}_{\text{org}} \sim 50\%$ )  $\text{POC}_{\text{non-fossil}}$  from the terrestrial biosphere from radiocarbon-dead  $\text{POC}_{\text{fossil}}$  from sedimentary bedrock. Using an end-member mixing model, we quantify the proportion of these POC sources and we find a significant presence of  $\text{POC}_{\text{fossil}}$  in Andean river POC, contributing a constant 0.37% to the solid suspended load mass and up to 80% of the total POC. By examining POC source during rising, peak and falling stages of floods we show that an enrichment of  $\text{POC}_{\text{non-fossil}}$  occurs during rainfall events, when erosion processes supply  $\text{POC}_{\text{non-fossil}}$  to the mountain river. Finally, the new data suggest that input of Andean  $\text{POC}_{\text{fossil}}$  can explain the presence of old POC ( $^{14}\text{C}$ -depleted) reported in the suspended load of the lower Amazon Basin, implying a greater persistence of Andean POC during fluvial transport than previously recognized.

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